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THE CRYSTAL STRUCTURE OF THE ARAGONITE PHASE OF CaCO_3

by

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The Crystal Structure
of the Aragonite Phase of CaCO_3

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Abstract

Aragonite (CaCO_3) crystallizes in the unit cell $\underline{a} = 4.9598(5) \text{ \AA}$, $\underline{b} = 7.9641(9) \text{ \AA}$, and $\underline{c} = 5.7379(6) \text{ \AA}$ at 25°C with four formula weights in space-group Pmcn. The structure has been refined to $\underline{R}_w = 0.024$, $\underline{R} = 0.040$ using 765 X-ray reflections from a single crystal. The Ca ion is coordinated to nine oxygens with Ca...O distances in the range $2.414(1) \text{ \AA}$ to $2.653(1) \text{ \AA}$. The two unique C-O distances in the CO_3 group are $1.288(2) \text{ \AA}$ (on the mirror plane) and $1.283(1) \text{ \AA}$. The two unique O-C-O angles are $119.62(4)^\circ$ (across the mirror plane) and $120.13(8)^\circ$.

1. INTRODUCTION

Aragonite (CaCO_3) is found in nature as a mineral and is an important biomineral because of its presence in coral, clam shells, gallstones and otoliths. It is isomorphous with the carbonates of large divalent cations such as Ba, Sr and Pb.

Aragonite is less stable than the calcite phase of CaCO_3 at room temperature, but is denser than calcite. This suggests that aragonite is more stable than calcite at low temperatures and/or high pressures. More details are available in reference 1. Because of the importance of aragonite, and because of the possibility of performing calculations on the lattice energies of selected carbonates along the lines suggested by Busing[2], we have collected new X-ray data from a single crystal of aragonite and have refined the structure from the positions given in 1924 by Bragg [3].

2. STRUCTURE DETERMINATION

FORMULA (ideal): CaCO_3 (aragonite phase); UNIT CELL: orthorhombic with $\underline{a} = 4.9598(5) \text{ \AA}$, $\underline{b} = 7.9641(9) \text{ \AA}$, $\underline{c} = 5.7379(6) \text{ \AA}$ at 25°C (calculated by least squares from 12 2 θ values observed on a diffractometer); volume: 226.65 \AA^3 ; radiation, $\text{Mo}(\text{K}_{\alpha 1})$, $\lambda = 0.70926 \text{ \AA}$; monochromator; highly

oriented graphite crystal; space-group: Pmcn; contents
4(CaCO₃); reciprocal lattice extinctions, hk0: $h + k = 2n + 1$,
h0l: $l = 2n + 1$; observed density, 2.947(2) g·cm⁻³ [4];
calculated density, 2.944 g·cm⁻³; CRYSTAL: material available
heavily twinned; small wedge largest single crystal fragment
found; this wedge was attached to thin borate glass fiber with
clear household cement; fiber attached to insert in goniometer
head with epoxy cement; origin of crystal, mineral sample
#75538 from National Museum of Natural History, Smithsonian
Institution, Washington, D. C. Supplied by J. S. White, Jr.;
linear absorption corrections made by 8 x 8 x 8 Gaussian
quadrature using subroutines written by C. W. Burnham [5]
and adapted by B. Dickens; maximum and minimum corrections
for absorption = 0.963 and 0.880 (transmission factors).
INTENSITY DATA: number of reflections, 2356 collected from 2
octants and merged into a unique set of 765, of which 619
are "observed" and 146 are "unobserved"; unobserved reflections
are those less than 2σ above background; maximum sinθ/λ for
data 0.907 Å⁻¹; method used to estimate data: θ/2θ scan,
scintillation counter; diffractometer; Picker 4-circle
single-crystal diffractometer automated by PDP 8/I computer
through FACS-1 interface and adapted to include least
significant digit of counts; COMPUTATION: setting programs,

those of reference [6] as adapted by Picker Nuclear Corporation; scan range: $1.4^\circ + 114.6 \frac{\Delta\lambda}{\lambda}$, $\Delta\lambda = 0.692$, $\lambda = 0.70926 \text{ \AA}$; scan parameters: backgrounds counted at higher and lower 2θ for 100 sec. each; $\theta/2\theta$ scan at $0.25^\circ/\text{min}$ for 2θ from one background position to the other; attenuators: 0.025 mm thick layers of Nb, 1 layer for first attenuator, 2 for second, 3 for third; scan range correction; table look-up method to obtain values recommended in reference [7]; paper tape processing program written by B. Dickens for Univac 1108 computer, contains adaptations of similar program by F. A. Mauer (NBS), standard reflection plotting routine and extinction reflection editing routine from programs by J. M. Stewart, University of Maryland; ^{this program} uses an intense standard reflection at low angle to correct for change in intensity of the primary X-ray beam. Counts in peak = $I = P - (T/2T_B) (B_L + B_H)$, $\sigma(I) = (P + (B_L + B_H) (T/(2T_B))^2)^{\frac{1}{2}}$, $F = ((AF)(LP)(I))^{\frac{1}{2}}$, $\sigma(F) = (\sigma(I)/2)(LP/I)^{\frac{1}{2}}$, where P = counts at the peak position, B_L and B_H = background counts at lower and higher 2θ respectively, T = time spent counting peak, T_B = time spent counting background, AF = attenuator factor, LP = Lorentz-polarization correction. Data merging program for equivalent reflections, written by B. Dickens for Univac ^{in this program} is ^{is} 1108 computer; each set of equivalent reflections/treated as

follows: Reflections which were all unobserved were averaged and given the largest individual standard deviation in the set. Unobserved reflections in the presence of at least one observed reflection were discarded. Observed reflections which, subsequent to this step, occurred only once in the list were copied unchanged but their standard deviations were increased by a factor of three. Observed reflections with magnitudes which agreed within the counting statistics and reflections with magnitudes whose ratios fell within the range 0.95 to 1.06 were averaged and given as standard deviation the maximum of the standard deviation from counting statistics and the standard deviation from the range estimate [8,9]. Under these circumstances, reflections whose magnitudes did not pass the criteria were discarded. If no reflections passed the criteria, the highest magnitude was taken and the associated standard deviation multiplied by five. The justification for these arbitrary increases of standard deviations is that without some corroboration, every reflection is suspect because of the possibilities of multiple reflection, including the "tail" of nearby intense reflections in its measurement, change in intensity of X-ray beam of crystal misalignment/etc. Scattering factors; those for

the neutral atoms in reference 10; least-squares refinements; full-matrix, with $\Sigma(w||F_O|-|F_C||)^2$ minimized; refinements include unobserved reflections which calculate higher than 2 σ above background; least-squares weights: $1/\sigma^2$;

$$R_w = (\Sigma(w||F_O|-|F_C||)^2 / \Sigma(w|F_O|)^2)^{1/2}, \quad R = \Sigma||F_O|-|F_C|| / \Sigma|F_O|;$$

thermal parameters have the form $\exp(-1/4(a^{*2}B_{11}h^2 +$

$$B_{22}k^2 + c^{*2}B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl).$$

Least squares and electron density synthesis calculations carried out with X-ray 67 system [11] of computing programs.

FINAL REFINEMENT: $R_w = 0.024$; $R = 0.040$, average shift/error for last cycle = 0.0017; standard deviation of an observation

$$\text{of unit weight} = (\Sigma(w(F_O - F_C))^2 / (765 - 28))^{1/2} = 0.775.$$

The highest peak in an electron density difference synthesis calculated after the final anisotropic refinement to $R_w = 0.024$ corresponded to about 1/3 of an electron and was about 0.95 Å from C towards O(1). The largest correlation coefficients are 0.34-0.44 between the scale factor and the B_{11} , B_{22} and B_{33} temperature factors of Ca.

The atomic parameters are given in table 1. The observed and calculated structure factors are given in table 2.

3. DESCRIPTION OF THE STRUCTURE

The structure of aragonite, the main points of which are well known, is shown in figure 1. The Ca ions lie in pseudo-hexagonal layers parallel to (001) and the layer sequence is

ABAB. The Ca layers are separated by CO_3 groups which lie in two layers parallel to (001), and form columns parallel to [001].

3.1. The Ca ion environments

The Ca ion lies on the mirror plane at $\underline{x} = 1/4$. Its environment is shown in figure 2 and summarized in table 3. The coordination contains three CO_3 edges, $0(1,2)$, $0(1^{\text{I}}, 2^{\text{I}})$ and $0(2^{\text{IV}}, 2^{\text{V}})$ and three apexes, $0(1^{\text{II}}, 2^{\text{II}}, 2^{\text{III}})$. The apparent thermal motion of Ca is almost isotropic, (table 1, Fig. 2).

3.2. The CO_3 group

The dimensions of the CO_3 group are given in table 4. All C-O distances in the CO_3 group are essentially equal with an average of 1.286 Å. This agrees well with the C-O distance of 1.283(2) reported [12] for calcite. There appears to be some significant deviation from trigonality in the angles; the reported angle of 119.62° for $0(2)\text{-C-}0(2^{\text{I}})$ is consistent with the $0(2, 2^{\text{I}})$ edge of the CO_3 group being coordinated slightly more strongly to Ca as judged from the Ca...O distances. If the apparent thermal motions of the atoms in the CO_3 group are attributed to thermal motion rather than to slight positional disorder, there seems to be oscillation within the CO_3 layer, i.e.,

more or less perpendicular to the edge coordination to Ca. Similarly, O(1) may be undergoing some additional wagging out of the CO₃ layer.

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Table 1 Atomic Parameters in Aragonite (CaCO_3)

| Atoms | \underline{x} | \underline{y} | \underline{z} | $\underline{B_{11}^*}$ | $\underline{B_{22}}$ | $\underline{B_{33}}$ | $\underline{B_{12}}$ | $\underline{B_{13}}$ | $\underline{B_{23}}$ |
|-------|-----------------|-----------------|-----------------|------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Ca | .25000 | .58507(5) | .25974(6) | .664(9) | .599(9) | .601(9) | .0000 | .0000 | -.01(1) |
| C | .25000 | .2386(2) | .4148(3) | .75(5) | .85(5) | .46(5) | .0000 | .0000 | .07(5) |
| O(1) | .25000 | .0770(2) | .4043(2) | 1.50(5) | .54(4) | 1.04(4) | .0000 | .0000 | .03(4) |
| O(2) | .4737(2) | .3196(1) | .4131(2) | .71(3) | 1.03(3) | 1.02(3) | -.32(3) | -.02(3) | -.09(3) |

Figures in parentheses are standard errors in last significant figure quoted, and were computed in the final cycle of full-matrix least-squares refinement.

* Thermal parameters are in \AA^2

[illegible]

Table 3

The Ca environment in aragonite (CaCO_3)

| Atoms | Distance, Å |
|--|-------------|
| Ca, O(1 ^{II}) | 2.414(1) |
| Ca, O(2 ^{II} , 2 ^{III}) | 2.445(1) |
| Ca, O(2, 2 ^I) | 2.520(1) |
| Ca, O(2 ^{IV} , 2 ^V) | 2.544(1) |
| Ca, O(1, 1 ^I) | 2.653(1) |

In all tables of interatomic distances and angles, the figures in parentheses are standard deviations in the last digit and were calculated from the standard deviations in the atomic positional parameters and the unit cell parameters.

Table 4

The CO₃ group and its environment in aragonite (CaCO₃)

| Atoms | Distance, Å, or angle, deg. |
|---|-----------------------------|
| C, O(1) | 1.288(2) Å |
| C, O(2) | 1.283(1) |
| O(1), O(2) | 2.229(1) |
| O(2), O(2 ^I) | 2.219(1) |
| O(1), C, O(2) | 120.13(8) ° |
| O(2), C, O(2 ^I) | 119.62(4) |
| O(1), Ca ^V | 2.414(1) Å |
| O(1), (Ca ^{II} , Ca ^{III}) | 2.653(1) |
| O(2), Ca | 2.445(1) |
| O(2), Ca ^{II} | 2.520(1) |
| O(2), Ca ^{IV} | 2.544(1) |

Figure legends

1. A stereoscopic illustration of the crystal structure of aragonite (CaCO_3). A unique set of atoms is labelled. The origin of the crystallographic coordinate system is marked by *.
2. The Ca environment in aragonite (CaCO_3). The labels refer to atoms in table 3.
3. The CO_3 group environment in aragonite (CaCO_3). The labels refer to atoms in table 4.

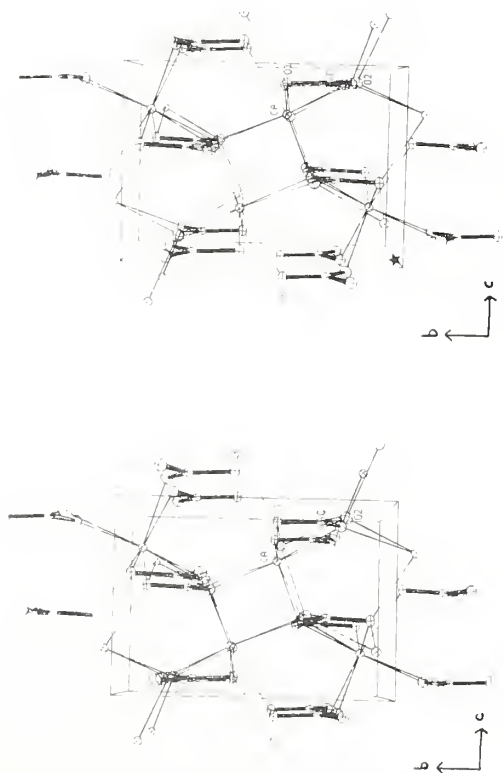


Fig 1

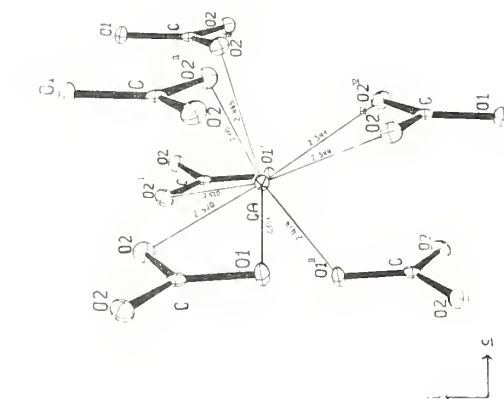


Fig 2

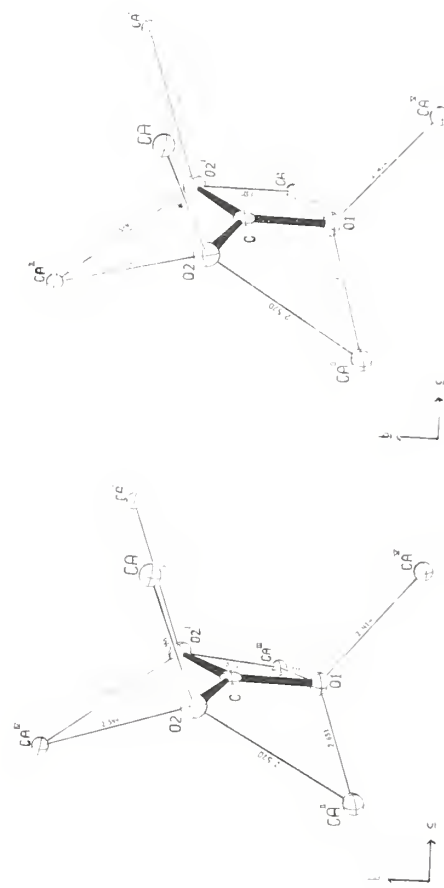


Fig 3

